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# Guidelines for the Procurement of Aerospace Nickel Cadmium Cells

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## ABSTRACT

NASA has been using a Modular Power System containing "standard" nickel cadmium (NiCd) batteries, composed of "standard" NiCd cells. For many years the only manufacturer of the NASA "standard" NiCd cells was General Electric Co. (subsequently Gates Aerospace and now SAFT). This standard cell was successfully used in numerous missions. However, uncontrolled technical changes, and changes in industrial restructuring require a new approach. General Electric (now SAFT Aerospace Batteries) had management changes, new manufacturers entered the market (Eagle-Picher Industries, ACME Electric Corporation, Aerospace Division, Sanyo Electric Co.) and battery technology advanced. New NASA procurements for aerospace NiCd cells will have specifications unique to the spacecraft and mission requirements. This document provides the user / customer guidelines for the new approach to procuring of and specifying performance requirements for highly reliable NiCd cells and batteries. It includes details of key parameters and their importance. The appendices contain a checklist, detailed calculations, and backup information.

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## EXECUTIVE SUMMARY

During the last 30 years the overwhelming majority of NASA missions have successfully used nickel-cadmium (NiCd) batteries for satellite energy storage systems. In the recent past, changes in the marketplace have dictated changes in the way NiCd aerospace cells and batteries are manufactured. Many of the changes are of a technical nature caused by events such as the exhaustion of the nylon separator material, the change in source for nickel powder, and other changes which have not been officially documented. The net result is that documentation referring to a "Standard" cell or battery have lost much of their usefulness. Additionally, anomalous battery performance of on-orbit satellites led NASA to reconsider the approach to the specification and procurement of NiCd flight batteries.

In 1992, Acting NASA Deputy Director Aaron Cohen convened a Battery Review Board to investigate the anomalous performance of NiCd cells on NASA spacecraft batteries in orbit. Specifically, the board was to determine the causes of non-uniform in-orbit cell performance in the Gamma Ray Observatory (GRO) and the Upper Atmosphere Research Satellite (UARS) and to suggest solutions to avoid these problems in the future. One of the Board's general recommendations was for NASA to move away from the use of the NASA standard cell and battery specifications detailing the requirements for manufacture and to let the individual cell manufacturers assume more of the responsibility for the quality of their product.

The specific Battery Review Board recommendation was to replace the specifications for the NASA Standard Cells with a Guidelines document to provide information on how the cells are manufactured and what are the critical design concepts to consider. A Guidelines document would aid in the preparation of a cell specification document for a specific mission and allow the individual Flight Projects to evaluate the cell vendor's cell manufacturing procedures and capabilities.

This document provides a complete description of the NiCd manufacturing processes, typical variability in the manufacture of the positive and negative plaques and plates and a functional description of the chemistry involved. Initially a historical description of the evolution of the NASA "Standard" cell is presented. Subsequently new technical advances such as the "super NiCd" and fiber pasted electrode technology are addressed in the text. This document also provides a description and rationale for the fabrication of the cell components, electrolyte filling process, and cell assembly. It provides recommendations for cell pre-acceptance tests, acceptance tests, and customer acceptance tests. It describes the roles of the Quality Assurance functions, the Defense Contract Management Command (DCMC) and customer quality. Travelers, data sheets and inspection reports are also addressed. Finally a checklist is provided to facilitate preparation of a NiCd specification.



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## SECTION 1

### INTRODUCTION

#### 1.1 OBJECTIVE

This document is intended to provide information and data that will facilitate the preparation of specifications for the procurement of nickel-cadmium (NiCd) cells to be used for spacecraft applications. In addition, it is intended to provide information on key characteristics and properties of the NiCd cell and battery to educate the reader and avoid potential problems and pitfalls. The aerospace NiCd cell is hermetically sealed, is of prismatic design, and is not to be confused with commercial design nickel-cadmium cells. The cell design acceptable for use in a space application must have completed an acceptable qualification test. That is, the cell design must have been previously used for a space mission or have been approved for use on a spacecraft. Subsequent to the successful use, the cell can be qualified by similarity for missions with identical or lesser requirements.

Four major specifications have been used for aerospace batteries for the past 25 years (Refs. 1–4). It is suggested that those not familiar with the basics of sealed nickel-cadmium cells or the history of NASA experience with NiCd cells read Reference 1 (*Handbook for Handling and Storage of Nickel Cadmium Batteries: Lessons Learned*). Based on past experience, it is considered necessary that, inspection of components, cells, and batteries and the processing thereof be performed. In addition to on-site Defense Contract Management Command (DCMC) inspection, it is strongly recommended that a Quality Assurance (QA) representative from the NASA or Air Force contractor provide oversight at the facility at least part time.

The information and data in this document are directly applicable to NiCd cells currently in production by cell manufacturers in the United States, Europe, and Asia. Information on new or advanced designs is discussed in Section 10.

#### 1.2 HISTORY / BACKGROUND

In the mid 1970s NASA instituted a program to develop a line of standardized equipment that could be easily duplicated for different NASA missions at reduced cost. Several items were included in this activity, e.g., Attitude Control (ACS), Computer and Data Handling (C&DH), Tape Recorder, and Modular Power Subsystem (MPS). It was determined that the NiCd cell and battery could be considered in this category. To this end the NASA Goddard Space Flight Center (GSFC) was assigned the task, and the battery specialists prepared *The Specification for the Manufacture of Nickel-Cadmium Aerospace Cells*, Number 74-15000, dated 1974 (Ref. 3). The cell, being the basic and most complicated item, was addressed first before the battery.

Four NiCd manufacturers responded to a NASA solicitation: General Electric (G.E., later Gates, and now SAFT), Eagle-Picher, SAFT America (previously Gulton Industries), and Yardney. Each was given an opportunity to prepare a Manufacturing Control Document (MCD) describing the complete process from incoming materials through manufacture, inspection, and test and including all inspection reports, data sheets, and travelers. Upon completion, each company was given the opportunity to manufacture 50 20-Ah cells. Three packs were to be tested at Crane in simulated low Earth orbit (LEO) regimes at 10, 20 and 30°C at 40% depth of discharge (DOD) and one at 25% DOD and 20°C. A fifth pack of five cells was to be tested in a simulated geosynchronous Earth orbit (GEO) regime at 60% DOD. Twenty five cells were to be made available to be selected for a 22-cell battery. Two cells were delivered dry for historical purposes and future evaluation if necessary.

Of the four manufacturers, only General Electric cells met all the specification requirements, which included individual plate tests, analyses, reduction of active material and increased electrolyte as well as

other specifications never before required. NASA termed the G.E. cells the NASA Standard Cell. It was referred to by a specific cell model number (42B024AB20/21) and manufacturing control document (MCD) number.

Meanwhile, McDonnell Douglas (MDAC) was awarded a contract by GSFC to develop the MPS for the first Multi-Mission Modular Spacecraft (MMS). This first spacecraft was the Solar Max Mission (SMM). MDAC was responsible for assembling a Battery MCD (BMCD) with the same objective as the Standard Cell. MDAC produced a 22-cell battery with the G.E. cells and performed all of the electrical and qualification tests required by the GSFC prepared Battery Specification (Ref. 4). All tests were completed satisfactorily. The SMM, using three 22-cell batteries in parallel, was successful in that it completed 8 years of operation (40,000 charge/discharge cycles) including a repair mission after four years. In the eighth year the solar arrays were jettisoned, and the battery discharged to failure. The batteries demonstrated a capacity of 16 Ah of the original 24. 50-Ah batteries patterned in the same way were manufactured and launched in Landsat 1 and 2, Earth Radiation Budget Satellite (ERBS), and (more recently) Gamma Ray Observation (GRO) and Upper Atmosphere Research Satellite (UARS).

Unfortunately, during the 1980s several manufacturing changes took place at Gates Aerospace Batteries. The replacement of the 74-15000 document with the NASA Handbook NHB 8073.1 (Ref. 3) removed some of the requirements in the 74-15000 making it easier for the manufacturer. The QA functions were severely reduced as well. The proprietary plate manufacturing processes, open only to specifically designated NASA individuals, were changed on several occasions. The availability and the source of the separator were also changed. During the NiCd GATES cell mini-workshop at MSFC (6/26-28/1988) a NASA task team review implicated changes in the proprietary negative plate process. Without data substantiating the many changes or the effect of the changes on long term performance, the quality and reliability of the Standard became questionable.

In 1992 NASA management became aware of the problems in the GRO and UARS batteries and raised concerns for future NASA missions, especially with the TOPEX and Mars Observer near-term missions. A NASA Battery Review Board was established by NASA Acting Director Aaron Cohen to assess the problem. The Chairman, Chet Vaughn of Johnson Space Center, and representatives from the other NASA Centers visited manufacturers, users, and NASA installations to better understand the problem.

One of the recommendations of the Board was elimination of the NASA requirement for the *NASA Specification for the Manufacturing of Aerospace Nickel Cadmium Storage Cells* (Ref. 3). JPL was given the responsibility of preparing a Guidelines Document to facilitate the preparation of specifications by individual companies and individuals interested in purchasing nickel-cadmium cells for aerospace use. This document is in response to that action item.

Regardless of cell size, type, or chemistry, specifications will be required, and manufacturers will need to describe their design and processes in a document equivalent to an MCD. Furthermore, many of the "lessons learned" with respect to the manufacture of NiCd cells are documented in the references cited above (Ref. 1-4), and they should also be consulted when evaluating a procurement for aerospace NiCd cells.

In recent years, NASA NiCd cell procurements were specified by the NASA Specification 74-15000 (Ref. 3), and NASA Handbook NHB 8073.1 (Ref. 4). Incorporated in these documents was a NASA requirement that the cell manufacturer have an MCD describing in detail all manufacturing operations starting with plate delivery to the aerospace facility, and all QA inspections for these operations. In addition there was a second MCD, unique to the procurement, that contained "travel cards," specifications, and drawings. It is expected that in the future there will be changes in the format and extent of MCDs and that these will also vary with the manufacturer. It is not clear at this time what the "MCD" of the future will be, but it must at least contain or reference all of the information contained in previous NASA "MCDs."

## SECTION 2

### TECHNOLOGY

#### 2.1 CELL DESIGN

The NiCd cell used for space applications must be hermetically sealed to prevent electrolyte leakage. So-called "sealed cells" or cells that have relief valves are not acceptable for space applications. Experience has shown that ceramic to metal seals (used to insulate the electrode terminals from the stainless steel case) prevent leakage of the aqueous potassium hydroxide (KOH) electrolyte solution and have demonstrated high reliability beyond 10 years. Terminal seals that use silver braze are not acceptable since they have been shown to result in silver migration leading to high resistance shorts across the ceramic insulator. High resistance shorts can lead to inefficient charge, high self-discharge and shortened life.

Within the sealed nickel-cadmium cell case is the "cell pack." The "pack" consists of several positive plates (positive electrode) alternating with several negative plates (negative electrode) and separators in between. Each positive plate consists of a porous (~80%) nickel 'plaque' filled with nickel hydroxide  $[\text{Ni}(\text{OH})_2]$  active material. Similarly, each negative plate consists of a porous nickel plaque except that the active material in the plaque is cadmium hydroxide  $[\text{Cd}(\text{OH})_2]$ . A non-woven nylon separator found between the plates (sometimes in an envelope form around the positive plates) is used to physically maintain plate separation and yet serve as a sponge to contain the electrolyte contact between plates. The nickel tabs of all positive plates are welded into a 'comb subassembly' to place the plates in an electrically parallel configuration. The negative plates are also welded to a "comb subassembly" in the same manner. The "cell pack" with combs at the top is then inserted into a stainless steel (SS 304L) case. A polyethylene wrapper is used to insulate the pack from the stainless steel case. The ceramic to metal seals, containing positive and negative terminals mounted into the stainless steel cover, are then welded to the positive and negative "comb subassembly."

To activate the cell, electrolyte must be added through the fill tube in the cover. Aqueous KOH having a concentration of 31% (this may vary in advanced designs) is the electrolyte. A sealed cell is sometimes referred to as a "starved" cell as compared to a "flooded" cell such as those used in vented NiCd aircraft batteries. The amount of electrolyte used in a sealed cell is critical. If there is too much electrolyte, the plates become flooded during overcharge resulting in poor oxygen recombination and high internal cell pressure. If too little electrolyte, contact with the active material will be reduced resulting in a loss of delivered capacity, higher internal resistance, and reduced performance. Some manufacturers may use additives in the electrolyte. These additives are often considered proprietary and are not identified in the documentation.

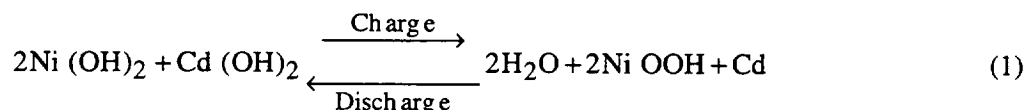
It has been found that non-woven nylon is an excellent separator material since it permits oxygen diffusion between the two electrodes, can retain large quantities of electrolyte, and is relatively inert to the KOH electrolyte. Non-woven nylon under the trade name of "Pellon" was used in most NiCd cells. More recently, a change in the process and the manufacturer name to Freudenberg, resulted in a new product line that is presently being evaluated for use in NiCd cells. Nylon, a polyamide material, has the disadvantage of increasing degradation as a function of temperature leading to reduced performance and life. The electrode reactions are also sensitive to temperature. These are the reasons low temperature constraints are utilized when storing or operating NiCd cells. At temperatures of  $0^\circ\text{C} \pm 20^\circ\text{C}$  nylon shows little degradation, but at temperatures above  $25^\circ\text{C}$ , in an oxygen environment, degradation becomes significant especially for long LEO and GEO missions. Sealed NiCd cells using "PBI/zircar" (polybenzimidazol/zirconium oxide) and PBI/polypropylene separators are also being manufactured to avoid the nylon degradation issue. These will be discussed further in the advanced design section.

The NiCd cell can be charged and discharged for thousands of cycles because of highly reversible electrode reactions. Actual cycle life is a function of temperature and DOD. A cell was thought to be of good quality if it would pass the NASA stress test consisting of two years of cycling (12,000 LEO cycles) at 20°C and 40% DOD. Cells that passed this test and were subsequently flown lasted for several years at the lower temperatures and DOD usually experienced on spacecraft. It can be operated in the totally sealed condition because the gaseous oxygen that is unavoidably generated at the nickel hydroxide plates (positive electrode) reacts with the charged cadmium plates (negative electrode) thus avoiding accumulation of gas within the sealed cell. To accomplish this, the oxygen gas must come in contact with the charged cadmium plate.

Although the design of the NiCd cell appears relatively simple, the overall electrochemical, mechanical, and thermal design parameters interact. The sensitivity to these makes some of the difference between a long-life reliable aerospace-quality cell and a commercial NiCd cell.

## 2.2 ELECTROCHEMICAL REACTIONS AND DESIGN

The overall chemical reaction in the cell is:



where

Ni(OH)<sub>2</sub>, (Nickel hydroxide) is the discharged positive active material

Cd(OH)<sub>2</sub>, (Cadmium hydroxide) is the discharged negative active material

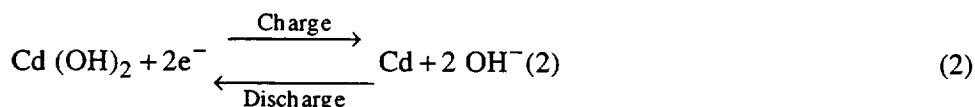
H<sub>2</sub>O, (Water) is produced during charge and used up during discharge

NiOOH, (Nickel oxyhydroxide) is the charged positive active material

Cd, (Cadmium) is the charged negative active material

When a cell is built, the active material in both electrodes is in the hydroxide form. As the cell is charged, the active materials are converted as shown in the reaction above. The net reaction involves production of water which reduces the electrolyte concentration by 4 – 6% at charge to full discharge. The reverse occurs during discharge as shown.

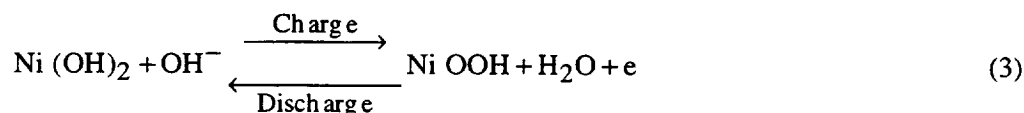
At the cadmium (negative) electrode the reaction can be expressed as:



e<sup>-</sup> indicates a free electron

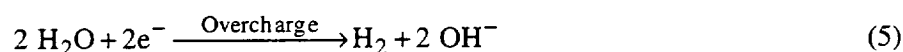
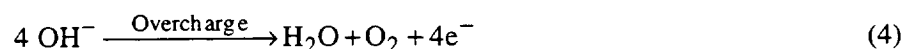
OH<sup>-</sup> is a hydroxyl ion from the ionization of KOH (K<sup>+</sup> + OH<sup>-</sup>) in solution

At the nickel (positive) electrode the reaction can be expressed as:



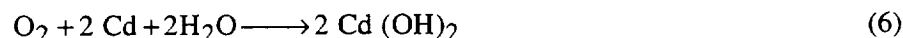
From individual electrode reactions (equations 2 and 3) it can be seen that the simple stoichiometry within the NiCd cell during charge is simply the transfer of hydroxyl ( $\text{OH}^-$ ) ions from the negative plates to the positive plates and the reverse during discharge. Equation 2 shows that electrons from the power supply are used to convert the  $\text{Cd}(\text{OH})_2$  to Cd as  $\text{OH}^-$  is released into the electrolyte. The  $\text{OH}^-$  at the positive plate surface reacts with the  $\text{Ni}(\text{OH})_2$  to produce the charged species,  $\text{NiOOH}$ , release water and produce electrons which return to the power supply, thus closing the circuit. It is interesting to note that the reduced concentration in electrolyte during charge is opposite to that associated with the familiar lead-acid cell.

When both electrodes are fully charged, all of the  $\text{Ni}(\text{OH})_2$  has been converted to  $\text{NiOOH}$ , and all of the  $\text{Cd}(\text{OH})_2$  has been converted to Cd. No further chemical change within the plates is possible. However, if the power supply continues to force electrons through the cell, i.e., into the negative electrode, returning from the positive electrode, the following 'overcharge' reactions will take place.



Note that the  $\text{NiOOH}$  and Cd are effectively unchanged during the process

According to equations (4) and (5) electrolysis of water (oxygen and hydrogen gas generation) will occur. (Actually some oxygen is formed at the nickel plates during a normal charge; however, it generally reacts rapidly at the Cd plates and is unnoticeable.) The successful operation of the sealed nickel-cadmium cell is dependent on keeping the cadmium plate from becoming fully charged so that equation (5) never takes place. This is possible by the simple design criteria of assembling the cell with an excess of charged cadmium active material so that the oxygen released at the nickel electrode can react with the cadmium at the cadmium plate, and excess uncharged  $\text{Cd}(\text{OH})_2$  to suppress the hydrogen-generation reaction.



Equation (6) shows that oxygen is discharging the cadmium active material during overcharge of the cell. The reaction of oxygen with cadmium not only prevents the cadmium electrode from reaching a fully charged state, but it also prevents an accumulation of oxygen within the cell. Hydrogen gas (if formed) will accumulate rapidly (2.4 mAh/cc) and produce high pressure which can actually burst a sealed cell (also see Appendix E). It should be noted that if the sealed cell leaks, oxygen will be lost, and the cadmium plate may reach a fully charged state and thus  $\text{H}_2$  evolution is possible, and the end-of-charge voltage will increase.

If the flow of electrons is reversed (i.e., during discharge) and the load continues to drain the cell, it is possible to drive the electrode reactions into polarity reversal ('overdischarge') and thus electrolyze water. In the case of cell reversal, the oxygen is evolved at the negative electrode and hydrogen at the positive electrode; this is the reverse of overcharge. If there is an excess of negative active material (generally the case) the hydrogen will be generated at the same rate as on overcharge.



In addition to permanent cell failure, cell reversal can result in cell can bulge and/or rupture in a short time (depending on discharge current). At spacecraft rate (normally 2 hour discharge rate) it can occur rapidly.

## 2.3 MECHANICAL DESIGN

The internal resistance of the cell is affected by the spacing and the quantity of electrolyte between the nickel and cadmium plates. Therefore, this dimension should be minimized. However, it is necessary to prevent any shorting between the plates; therefore, there must be a compromise to keep resistance low and guard against shorting. The controlling factors are separator thickness, separator compressibility, and the pressure to restrain the cell pack thickness. The thickness of the cell case and external pressure exerted on the cell are also factors.

The headspace "free volume" of the cell is defined as the void space between the plates and the cover. This also is a compromise. The gas pressure during overcharge is inversely proportional to the free volume within the cell, and thus if minimized, will result in a somewhat higher pressure. However, a large space will significantly affect the total cell weight, which is a significant factor in specific energy (Wh/kg).

The wall thickness of the cell case is another tradeoff. The cell pack must be kept constrained on its flat surface in order to maintain consistent continuity between plates. In the past, case thicknesses of 0.48 mm (0.019") were common, but 0.30 mm (0.012") has also been used. In larger cell designs, e.g., 50 Ah, the bulging of the narrow edge of the cell became a concern. Structural analysis of this problem at GSFC in the 1970s resulted in recommended corrugations along the case side wall, which provided beam-like strength and prevented bulging there. To prevent bulging in the large flat surface requires external battery support, e.g., endplates. An outer aluminum case or "retainer" has been used to support the stainless steel case and provide better heat transfer than stainless steel. (Aluminum has ten times the heat conductivity of stainless steel.)

The design of the metal-to-ceramic seal is both a mechanical and electrical factor. The terminals must not be stressed or distorted so that the seals remain intact. When the terminal seals were downsized on one cell design, it was necessary to add cover reinforcement to compensate for the lost support of the larger terminals. The corrugations were also used for cell cover support to prevent bulging. It must be understood that sealed nickel-cadmium cells are never operated without mechanical support of the large faces, but edges and bottoms are sometimes unsupported.

## 2.4. THERMAL DESIGN

It has already been mentioned that the use of nylon separator material places a constraint on the temperature limits for sealed nickel-cadmium cells. The cadmium plate is also temperature sensitive, and the solubility of cadmium becomes an important factor when the temperature exceeds about 30°C. The nickel electrode is also sensitive to temperature and does not charge efficiently at temperatures greater than 30°C.

For thermal reasons, sealed NiCd cells are usually limited to about 2.5 cm (1") in thickness. Cells used for non-aerospace applications have been manufactured with thicker designs (more plates in parallel), but thermal control is more difficult to maintain.

For both thermal and electrical reasons, sealed cells are optimized when the plate width and height are about equal. This gives a lower voltage drop across the plate and gives slightly improved temperature control.

The loss of thermal control (thermal runaway) has caused some failures, but it has seldom, if ever, been caused by the cell design. Thermal runaway results from the fact that as cell temperature increases, cell charge voltage decreases. When the power source voltage remains fixed (voltage-limit charging), and there is no current limit, the battery charge current will continuously increase and heat the cell, generate high pressure and destroy the nylon separator. Failures have resulted from charge control malfunction or inadequate thermal design of the battery and the spacecraft thermal control system.

## SECTION 3

### CRITICAL CELL DESIGN CONSIDERATIONS/FACTORS

Some critical design factors have already been mentioned above. However, in this section they will be reviewed and connected with problems that have occurred in the past. Appendix D has a table of critical parameters that are typical for various manufacturers. These values may vary according to the specific cell design.

#### 3.1. QUANTITY OF ELECTROLYTE

The quantity of electrolyte has probably caused the most serious problems in long term reliability of NiCd cells. As mentioned above, excess electrolyte leads to flooding and high internal pressure, while minimal electrolyte results in reduced performance and shortened life. Performance of the NiCd cell depends on electrochemically efficient and reversible reactions directly involving the electrolyte. Manufacturing designs have emphasized the specific energy (Wh/kg) of the NiCd cell and battery and thus have resulted in reduced quantities of electrolyte to minimize weight. In addition, excessive active material loading of the plates to achieve higher capacity has resulted in reduced porosity where electrolyte is housed. The design should contain the greatest amount of electrolyte possible without exceeding internal pressure during overcharge of about 65 psig (240 kPa). A rule of thumb for aerospace NiCd cells is 3 cc of electrolyte per ampere hour of nominal capacity, higher in some of the newer designs as discussed in Appendix D. Teflon coating of the negative plates has resulted in less flooding of the cadmium and thus an opportunity to maximize the electrolyte. In summary, the quantity of electrolyte to be added to a cell is affected by:

- (a) Porosity of the plates
- (b) Separator retention of electrolyte and oxygen permeability
- (c) Nickel active material morphology
- (d) Negative plate Teflon treatment
- (e) Free volume
- (f) Inter electrode spacing (IES)

All of the above factors have been varied during recent years, and the interaction has in some cases caused low electrolyte fill resulting in limited cell life. In some cases there has been a drying out and actual charring (burning) of the separator.

#### 3.2 CADMIUM PLATE DEGRADATION

The cadmium electrode is known to lose capacity with cycling. If, in the early stages of cycling, the cadmium electrode were to reach full charge close to that of the positive electrode, ultimately (with continued cycling), the cadmium electrode would degrade, and the cell would become limited by the negative electrode on charge. This is due to chemical changes in the cadmium electrode during cycling, which result in degradation and loss of capacity. The result of being negative-limited on charge is premature hydrogen gas evolution. Likewise, if the negative electrode capacity is initially limiting the discharge, the cell capacity will continue to decrease because of the cadmium electrode degradation. Degradation rates are affected by:

- (a) Electrolyte volume
- (b) Temperature

- (c) Rate of charge and discharge
- (d) Plate construction and loading of the active material
- (e) Nylon hydrolysis

The cause for this degradation and the differences between plate and cell lots is not well documented. Recommended corrective action is to establish an acceptable degradation rate and employ a plate "stress" test on sample plates from each lot to assure conformance. A 20-cell cycling test of sample negative plates incorporated in the GSFC 74-15000 NiCd cell and Battery Manufacturing Specification (Ref. 3) provided information on the plate degradation.

### **3.3. NEGATIVE TO POSITIVE RATIO**

The negative-to-positive ratio is a design factor related to the balance between charged and discharged active material in both electrodes and the unequal degradation of the positive and negative electrodes. Cadmium plate capacity, for various reasons, decreases during life, and even with a defect-free optimum design, it will probably be the life-limiting factor. Lower temperature,  $0^{\circ}\text{C} \pm 5^{\circ}\text{C}$ , appears to be the only method of extending cadmium plate life. This ratio is included as a critical parameter in Appendix D.

In order to suppress hydrogen evolution on the negative plate at the end of charge, additional discharged negative active material  $\text{Cd}(\text{OH})_2$  is required so that when the positive electrode reaches full charge there will be ample negative active material to charge, and oxygen will recombine at the negative electrode safely as the electrode charges. The term is "positive-limited" on charge.

In addition, excess charged negative active material must be available when the positive electrode is fully discharged. This condition is known as "positive-limited" on discharge. The reason for this condition is that the negative electrode tends to degrade faster than the positive electrode especially when it is fully discharged each time. Therefore, the cell is designed to be "positive-limited" on discharge to avoid a continuous capacity reduction with cycling. This is only necessary if the cell is fully discharged. In low Earth orbit (LEO), the cells are rarely discharged more than 25% depth of discharge (75% of capacity left). Cells are designed to be "positive-limited" on charge and discharge.

For a sealed cell to operate for 10 or more years it is critical that the deliverable ampere hour capacity of the cadmium plate be at least 1.5 times the capacity of the nickel plate. The ratio is established during the loading of the plates and it must be confirmed by test prior to fabricating cells. 40% of the excess negative is discharge reserve (charged active material referred to as "precharge"), and 60% of the excess is in the discharged condition for "overcharge protection." (See Figure 3-1 for a schematic of the NiCd cell design.)

The GSFC 74-15000 (Ref. 3) specification required a measurement of the negative:positive ratio after the first acceptance test and at the completion of the acceptance tests described below. This provided a measure of the ratio and the stability of the electrode balance.

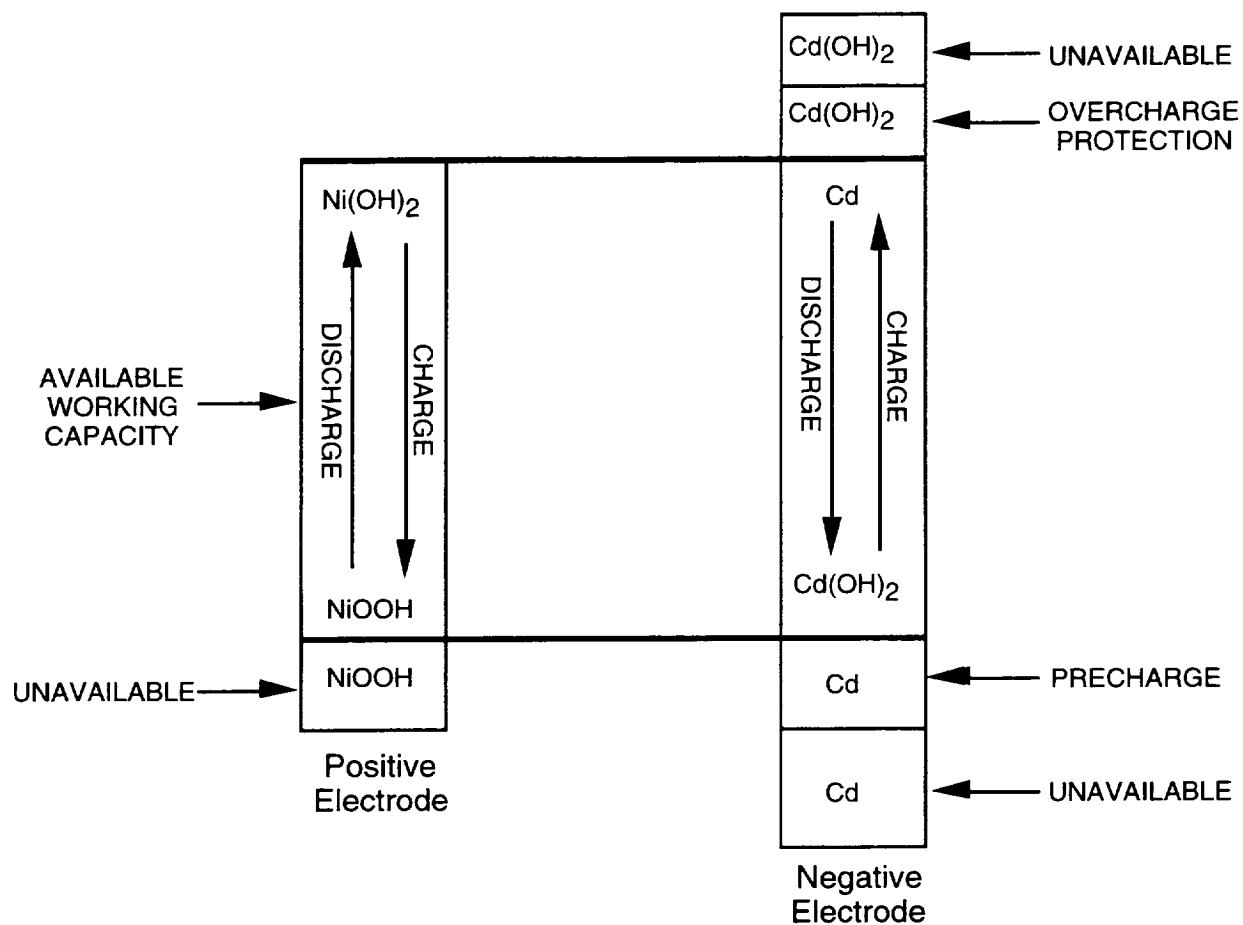
### **3.4 SEPARATOR MATERIAL**

For many years the separator material used in the aerospace NiCd cell was a non-woven nylon fiber material (~0.33 mm, ~13 mils) produced by an aqueous zinc chloride process, specifically, Pellon 2505 ML made by the Pellon Corp. However, there were concerns with the material handling and storage methods which resulted in premature cell degradation. These included:

- (a) Addition of a wetting agent to the nylon separator internal added to degradation
- (b) Inadequate washing to remove zinc chloride and other contaminants
- (c) Inadequate storage protection



Despite these problems, this material (selected in the 1960s under a NASA contract with Gould) was used almost exclusively in NASA missions. Missions using cells with this material operated successfully in space for more than 15 years.



**Figure 3-1. Diagram showing overcharge protection and precharge in a nickel cadmium cell.**

When the separator-manufacturing process was discontinued for environmental reasons, an effort was undertaken to find a suitable replacement. Currently non-woven nylon material is being produced by a hot gas method. The materials most closely resembling the original separator are designated 2536 and 2538 by the Freudenberg Company (replaces the Pellon name - parent company of Pellon). These have been undergoing testing to determine cell performance and effect on cell reliability.

New separator alternatives, Zircar and polypropylene will be discussed in Section 9.



## SECTION 4

### CELL MANUFACTURING PROCESS RECOMMENDATIONS

To assure consistency of the manufacturing process for an aerospace-quality NiCd cell capable of reliable performance and >10 year, >25,000 22% DOD LEO cycles operation, it is necessary for the cell manufacturer to document all incoming materials requirements and tests, process steps, testing and quality requirements. This was previously done by the use of a Manufacturing Control Document (MCD) prepared by and maintained by the cell manufacturer. A similar requirement for all future aerospace quality cell procurements is also necessary. The organized document giving manufacturing procedures with inspections, measurements and tolerances, quality control procedures, travel cards, references to all drawings and specifications, and copies of forms used (starting from incoming inspections to the final buy off of cells for shipment) is necessary to verify that the process was accomplished in the manner consistent with an aerospace-quality NiCd cell.

The manufacturing process should be summarized in a "Flow Chart" which indicates all steps in the process and identifies the inspection requirements by the manufacturer, by the Government Defense Contracts Management Command (DCMC), and by the QA Representative of the NASA contractor. The inspection points should be consistent with NASA approved mandatory inspection points.

The manufacturing process will vary between the cell manufacturers, but the critical factors in cell design for reliable performance and long life remain the same even if the process varies.

#### 4.1 PLAQUE MANUFACTURE

Plate making begins with a conductive inert "substrate," which may be a nickel plated, perforated steel ribbon approximately 0.05 mm (0.002 in.) thick or which may be a nickel screen about the same thickness.

The "plaque" can be produced by one of two methods, wet "slurry" or dry-powder process. In the "slurry" or "continuous" process, a continuously moving substrate is coated with a viscous slurry containing the nickel powder (produced by the carbonyl process by Inco). The 'slurry' consists of the nickel powder suspended in a uniformly mixed solution of water and a binder material, such as carboxymethyl cellulose or alternative. The moving coated substrate passes through a sintering furnace, where under a reducing gas atmosphere the nickel slurry is dried and reduced to form the nickel "sintered plaque." The plaques for the nickel and cadmium plates are identical, differing mainly in thickness. The positive and negative plaques in the form of a continuous strip and having a porosity greater than 80% are each wound in the form of a "spiral." A number of spirals, e.g., approximately seven, are layered on shelves and placed on a "post" ready for impregnation with active material.

The dry powder method, the substrate is placed in a mold over a layer of loose nickel powder, of the same type as above. The substrate is then covered with another layer of the nickel powder such that the substrate is in the center. The mold is then placed on a belt running through a three-stage reduction furnace to bond the nickel particles together into an >80% porous sintered plaque. The plaques for the nickel and cadmium plates prepared in large sheets (e.g., 25 cm × 25 cm, 10 in. × 10 in.) are identical except for thickness. They are then impregnated with the active material as described below.

Prior to the impregnation process, the sintered material designated for use as the nickel (positive) plates may be subjected to a "passivation" process, which consists of a heat treatment in air (or in water). The object is to oxidize the nickel plaque surface and reduce the nickel "attack" during the impregnation process. This process can also have a great effect on the quantity and distribution of active material in the plate (described below). The nickel oxide film produced on the surface of the nickel results in added cell resistance. Both of these may have a serious affect on performance and reliability.

The plaques from both dry and slurry processes are to be "coined" (nickel compressed) in an outline of the plate for the specific cell size required. When cut to size later, the plate edges will have less tendency to chip around the edge. Minimizing chips is important because chips could fall between plates and cause shorting in the cell. There needs to be some method for identifying plaques for positive plates differently from negative plaques. The identification needs to be carried through the entire process and into cell assembly.

## **4.2 PLATE MAKING (IMPREGNATION)**

There are several methods for impregnating the plaques with the cadmium hydroxide and nickel hydroxide active materials. The most familiar are the chemical impregnation and electrochemical impregnation methods. The process for producing the positive plates (plaques containing nickel hydroxide active material) is similar but chemically different from the negative plates (containing cadmium hydroxide active material).

### **4.2.1 Chemical Impregnation (Slurry Processed Plaques)**

The posts containing the plaques made from the "slurry" process designated as positive plates are impregnated with nickel nitrate and cobalt nitrate until a designed level of loading (uptake of solution into the pores) is reached. The goal for cobalt hydroxide is 6-8% of the total active material; however, it is usually on the order of 2-4%. The impregnation step is sometimes done under vacuum to achieve loading in the center of the plaque.

Because the nitrate solution is strongly acidic, a significant quantity of the nickel from the plaque dissolves into the nitrate solution, unless the plaque has been "passivated" (described above). The dissolving of the nickel plaque is referred to as "nickel attack." It has a major effect on the structural integrity of the plaque as well as the active material utilization. Although "passivation" is intended to avoid this problem, the pitfalls of "passivation" are also evident. Thus, the usefulness of "passivation" is still an unknown for NiCd cells.

The positive post is then immersed in a tank of sodium hydroxide to convert the nitrates to hydroxides. The post is then washed with water (deionized) to remove and wash away the nitrate solution and other solubles. It is imperative that all nitrates be removed to avoid the "nitrate shuttle" which in a sealed cell can result in a chemically induced short. The removal of nitrates must be confirmed by chemical analysis. The spirals in the post are allowed to dry, and then the post is weighed to determine the weight gain, which is related to the nickel hydroxide active material in the plaque. If inadequate to meet cell capacity requirements when the summation of the plates is considered, the post is placed in the nickel nitrate/cobalt nitrate solution and the process repeated. The process is repeated until the weight pick-up is indicative of the desired capacity, as many as seven times. In addition to the disadvantage of multiple steps, the active material may be deposited at the outer surface of the plaque, thus leaving large areas within the plaque without active material.

The negative impregnation process is similar to the positive process. The posts that are to become cadmium plates are impregnated with cadmium nitrate until a designed level of loading is reached. The impregnated posts are immersed in sodium hydroxide solution tanks to convert cadmium nitrate to cadmium hydroxide and then to wash away all nitrate solution. This is followed by washing with deionized water and drying. The removal of nitrates and other solubles is likewise necessary and must be confirmed by test. The process is also repeated as many as seven times to achieve the desired weight pick-up.

Samples of both plate materials are taken from each spiral on each post and sent to the laboratory for inspection, analysis, and test. These test data are critical to verify the loading, weight, thickness, porosity, and Ah capacity. The manufacturer should perform additional tests, such as the "Screening Test for

Cadmium and Nickel Plates” (Ref. 5). The data from all plate tests should be recorded on plate inspection forms and reviewed by the manufacturer QA, DCMC, and the Contractor QA before accepting the plates for an aerospace application.

#### **4.2.2 Chemical Impregnation (Dry Powder Processed Plaques)**

This process is similar to the slurry process except that the plaques to be impregnated are individual (25 cm × 25 cm, 10 in. × 10 in.) pieces capable of providing a number of plates when cut to the desired size. The plaques are impregnated with the nickel nitrate/cobalt nitrate solution as above. However, the conversion to hydroxide is performed in air, with the large positive plaques being electrochemically oxidized and the negatives being reduced as in the charge of the cell. The expected advantage is more efficient conversion to the hydroxide. The positive plate is not impacted by this process. But, in the case of the negative plates, the reduction results in the formation of cadmium metal, which can react with the oxygen in the air or in the drying ovens in the drying process. The recycling of the four-step process is continued until the weight pick-up meets the loading requirement as above.

#### **4.2.3 Electrochemical Impregnation**

Electrochemical impregnation became a viable process in the early 1980s using two separate processes, “aqueous nitrite” and “alcoholic.” These chemicals were used to maintain the pH of the solution at prescribed levels during impregnation and thus control the deposition process. Although they have been adopted for both positive and negative electrodes, most experience is with the positive (mainly because of the interest in these plates for nickel-hydrogen cells). In addition, the electrochemical impregnation process has been tried with the slurry and dry powder processed plaque. The process offers several significant advantages. First and foremost it is a one-step process requiring the electrochemical reduction of nickel nitrate to nickel hydroxide directly. The ampere hours (capacity) passed during the polarization of the plaques are directly related to the deposited nickel hydroxide active material (cobalt is also co-deposited directly from the nitrate solution), and thus to the cell capacity. Secondly, because the deposition of the active material takes place at the nickel closest to the substrate, the hydroxide deposit fills the inside of the plaque before moving outward. This results in a plate with higher capacity per cm<sup>2</sup> than in the chemically impregnated plate. Another advantage is that because the deposition is at the nickel interface, there is more room for electrolyte which has been shown to enhance performance. After reaching the loading goal, the plate is washed, dried, and readied for cell preparation.

### **4.3 PLATE PROCESSING PREASSEMBLY**

If the plate materials are approved as acceptable, they are cut to the cell size dimensions. The NASA contractor QA representative and the DCMC representative must conduct a “customer plate buyoff,” which is to include a review the “Plate Acceptance and Inspection Report” for providing adequate information that the process in the “Manufacturing Control Document” (MCD) has been followed and the plates meet the criteria. This will be the basis for the decreeing that the plate material is acceptable.

The plate acceptance criteria should include two items. First, plate porosity should be >35% (plaque porosity - active material fill), or higher. Second, the cadmium plate measured capacity should be 1.5 times the nickel plate capacity. All other data should meet the manufacturer’s specification requirements. Both nickel and cadmium plates are inspected for defects such as: cracks, burrs, pin holes, edge coining, and surface condition which, would be indicative of a plates that were subject to stresses or were of poor design or quality to meet a long term mission. Criteria for acceptance based on visible and dimensional data are needed.

Following the “customer plate buyoff” and satisfactory passing of the visual acceptance criteria, the positive and negative plates are sorted according to weight. This is done to minimize cell-to-cell capacity variation. The average weight of each type of plate is established by weighing 100 plates. A simple method can be used for the sorting. Use two balances: one with average + 3.5% tolerance and the second

with average -3.5% tolerance. If the plate weighs less than the former and more than the latter it is acceptable. An alternate method is to weigh each plate and use a statistical approach in selecting plates so that each cell is similar in weight. Thickness screening is also necessary to avoid non-uniform compression within a cell and between cells. Usually, differences in thickness will be identified during the weight screening. A method for screening and selection of NiCd cell plates that is commonly used has been described in Ref. 6.

#### **4.4 FLOODED TEMPORARY CELL TESTING**

Although plate capacity was established from sample plates while still in the "plate-making" operation, all plates are to be placed in temporary flooded electrolyte cells to determine the capacity, help remove carbonate and other impurities, and bring all plates to their full state of electrochemical discharge. This temporary cell test will verify the negative:positive ratio is a minimum of 1.5 and determine if the electrochemical capacity expected is there. The testing is performed in inert containers with nickel and cadmium plates widely separated and flooded with 31% KOH. It is sometimes referred to as electrochemical cell testing (ECT). The data from the ECT testing is of utmost importance since the plates will afterward be committed for fabrication into sealed cells. Temporary cells must be rejected if they do not meet the negative-to-positive capacity ratio of 1.5 and the total cell capacity requirements.

The final step of the ECT operation requires that the negative electrode be discharged until capacity has been exhausted at a somewhat lower current to avoid corrosion. This may require over discharging the positive plate somewhat. Upon completion all plates are considered to be in the "ground" state (full electrochemical discharge).

After the temporary cells are dismantled, all plates are washed in deionized water and dried. Two treatments have been used at the conclusion of the ECT tests and cell dismantling. One of these is Teflon coating of the negative plate to allow additional electrolyte in the cell (and yet avoid flooding of the negative electrode), to reduce cadmium migration, and to reduce surface deposition. The coating of cadmium plates with a Teflon emulsion has been used to limit cadmium migration, which can become a problem for long term operation and when temperatures are above 30°C. Removal of carbonate on positive and negative plate surfaces is also accomplished to reduce inactive electrode area resulting in available capacity loss and non-uniform current flow. This can be done at this step or later as a cell pack. Positive and negative plates are then inspected 100% for visual defects, and the tabs are cut to the correct dimension for the sealed cell.

#### **4.5 SEALED CELL ASSEMBLY**

Some cell specifications require that nickel plates and cadmium plates are weight sorted so that each sealed cell will have approximately an average weight of both plates. Other specifications rely on the fact that random plate selection will result in average weight cells. Assuming the plaques to be relatively consistent in weight, the weight of a plate will be a function of its active material weight and therefore its plate capacity. Also, some cell specifications require that a set of nickel plates and cadmium plates be combined and that the combined thickness be measured under pressure. A tolerance on thickness is established, and a requirement can be set.

##### **4.5.1 Welding Cell Pack to Cover**

The inspected plates with the tabs cut to correct dimensions, are combined into cell packs having the correct number of alternate nickel and cadmium plates. The positive plates (possibly 10 - 30) are welded to one 'comb,' the negatives to another. In some cases the comb is already part of the cover assembly and in other cases the comb must be welded to the cover assembly after the plates have been welded to the comb. In any case, the plates are welded to the combs that are connected to the terminals. The welding is to be accomplished by tungsten inert gas (TIG) welding for minimum resistance and reliability, and it

must be done by a certified individual. The NASA contractor, QA representative, and DCMC individual should inspect the welding workmanship.

#### **4.5.2 Plate Treatment**

The assembly of plates and cover is then given a carbonate removal treatment to remove carbonate that has accumulated on the plates during handling. Potassium hydroxide, which is the electrolyte in both the temporary cell and the sealed cell, is very reactive with carbon dioxide in the environment as are the plate materials. The potassium and other carbonates produced are detrimental to long life, cell performance, and reliability.

#### **4.5.3 Separator Properties**

The separator material serves the dual function of providing mechanical separation and serving as a sponge to contain the electrolyte that is required for conductivity between plates. There are two approaches to installing the non-woven nylon separator material into the cell pack. One approach is to form bags by heat-sealing and fit every nickel plate with a separator bag. Another approach is to wind a continuous length of separator between the nickel and cadmium plates. In any, case there must be a separator between each nickel plate and cadmium plate.

The separator is generally compressible material that is reported by the manufacturer to have a thickness of 0.33 mm (13 mils) depending on measurement technique and instrument. When inserted in the cell, the separator is designed to be compressed by 0.05–0.08 mm (2–3 mils) to maintain conductivity between positive and negative plates when the electrolyte is added. However, it is well known that the positive plates (and negative to some extent) expand with cycling sometimes as much as 0.2 mm (10 mils). Therefore, the separator can be squeezed excessively resulting in movement of the electrolyte out of the separator and into the plates. This “separator dry-out” affects the long term operation of the cell. The expansion of the positives is due to excessive active material loading levels, which if reduced, minimize this problem.

In the past, separators from every cell and separator lot have been subjected to numerous analytical and characterization tests to identify long term reliability characteristics. Although these tests have provided useful information on the separator characteristics, no test or tests have proven to be a discriminator. The results of the separator tests (Separator Test Report) should be available for review by DCMC and the Contractor QA. This report will present the test results for weight, thickness, tensile strength, soluble impurities, insoluble impurities, etc.

#### **4.5.4 Pack Insertion and Tests**

After the separator is added to the cell pack, the pack is encased with the polyethylene insulator (wrapper) and subjected to an electrical “short” test while being subjected to a compression force exceeding that in the cell. This will detect any small metallic particles bridging through the separator or plate protrusions which could result in a short. The resistance between the cell terminals should be greater than 100,000 ohms. This test needs to be performed under minimum humidity conditions to avoid misinterpretation of results.

Cell packs having passed the “short” test are inserted into the stainless steel case. This should be a snug fit but the force to completely insert the cell pack into the case should be minimized. Some manufacturers may use a vibration plate to help keep the force required for plate pack insertion to a minimum. Others compress the plate pack including separator to minimize thickness. The separator will return to form once inside the cell.

Radiographic inspection of the unsealed cell should be done. Careful examination of the X rays could reveal foreign particles, misalignment of plates or tabs, or distortion of plate edges. If X rays are taken of

the cells, there should be a requirement that every X ray be studied carefully, since it is difficult to detect possible defects.

The TIG welding of cover-to-case is another critical operation and must be performed by a "certified" individual. There must be 100% inspection of the weld; pin holes which result in leakage from the sealed cell are not completely impossible. After the pressure gauge and valve assembly is attached to the fill tube, the cells are pressured with helium gas and allowed to stand for about 16 hours to determine if there is gas leakage. From this point the grouping of positive plates is referred to as the positive or nickel hydroxide electrode, and the negative plates as the negative or cadmium hydroxide electrode.

#### **4.6 CELL ACTIVATION**

The quantity of electrolyte to be used in the cell is determined by the responsible project engineer after a determination is made of the free volume of a sample cell. This quantity should be approved by DCMC and the NASA QA representative. If the identical cell design has been previously manufactured and tested, the quantity of electrolyte should be consistent, and a minimum/maximum tolerance can be established. As mentioned in Section 3.1, the quantity of electrolyte is extremely critical. The rule of thumb is 3 cc per ampere hour of nominal capacity as a minimum. Super™ and Magnum™ cells use  $\geq 4$  cc/Ah and the nominal capacity is the same as the nameplate capacity.

Cell weight should be recorded before filling with electrolyte. The actual addition of electrolyte should be made with an automatic micro burette. The cell should be weighed after the addition of electrolyte to verify that the correct amount of electrolyte was added to each cell. These data should be reviewed by the NASA QA representative. The gauge and valve assembly is reattached to the fill tube, and the cell is again pressurized with helium and let stand to check for leaks. The filled tube is cut to length, pinched-off and welded. This completes the cell fabrication.



## SECTION 5

### MANUFACTURER'S PRE-ACCEPTANCE TESTING

Sealed NiCd cells require a significant amount of operation before the cell stabilizes electrochemically. The initial cycles are "formation" cycles to convert the nickel hydroxide active material and cadmium hydroxide active material into the "beta" crystalline form. These "formation" cycles are a series of charge and discharge cycles with planned overcharge of each cell.

Following the "formation" cycles, the negative electrode "precharge" is produced. A procedure is used to adjust the cell active material balance to produce a small quantity of charged active material (cadmium) in the negative electrode (~40% of the excess negative electrode capacity). This excess charge is necessary to prevent fading of cell capacity and enhance the oxygen recombination rate as described in Section 2.2.

The procedure involves charging of the cell until the positive electrode reaches full charge then continuing the charge, thus generating and venting oxygen gas. Oxygen lost from the cell instead of recombining on the negative electrode will result in an imbalance in electrode capacity between positive and negative electrode. Consequently, when the cell is discharged to failure, the positive electrode will be limiting, and the charged cadmium remaining will be equal to the ampere hour equivalent of oxygen removed (4.4 mAh/cc-atm). The remaining excess negative active charge (~60%), when the positive electrode reaches full charge, is in the discharged condition used for "overcharge protection" to avoid hydrogen evolution.

The remainder of the cycling tests are aimed at determining the maximum cell capacity and the pressure during overcharge at 0° and 22°C. The pre-acceptance tests typically include the following:

- (1) 3 or more Formation Cycles at 22°C - complete discharge after each cycle.
- (2) Precharge of cadmium plate - oxygen is vented to a calculated ampere hour precharge determined by project engineer.
- (3) Overcharge test at 22°C for 48 hours.
- (4) 10 or more burn-in cycles at 22°C.
- (5) Overcharge Test at 22°C.
- (6) Capacity Test at 22°C.
- (7) Capacity Test at 0°C.
- (8) Overcharge at 0°C.
- (9) Capacity Test at 0°C.

The data from all of the pre-acceptance tests should be available to the NASA contractor QA representative and DCMC. Although the NASA procurement specification may not have specific requirements for all of the tests, the data must show that the cells meet all of the manufacturer's specifications or standards. The overcharge tests and the capacity tests at both 22°C and 0°C are very significant. In addition to verifying that all cells meet the minimum requirement, it has been very helpful to plot histograms of the end-of-charge voltages for the overcharge tests and the ampere-hour capacity for the capacity tests. These histograms should appear as reasonable "normal" distributions, and any cells appearing outside of a 3-sigma tolerance should be watched closely during the acceptance tests. These are helpful in selecting uniform cells for a 22-cell (28 V) battery used in spacecraft power systems.

Following the setting of the precharge (Item 2) at 2%, a minimum of two cells, from each lot should be removed from test and sent to the laboratory for analysis. This analysis should include:

- (1) Positive capacity to 0.5 volts (electrochemical)
- (2) Positive capacity to 0.0 volts (electrochemical)
- (3) KOH concentration and quantity
- (4) Carbonate concentration
- (5) Total negative capacity (chemical)
- (6) Total positive capacity (chemical)
- (7) Total precharge
- (8) Overcharge negative

The purpose of these tests is to verify continuity of the manufacturing process and materials used. A manufacturer's specification should include requirements for the overcharge negative and the total precharge. All of the data from the above list should be tracked from lot to lot. A procedure for analysis of NiCd cell materials is described in Ref. 7. The consistency of the manufacturing process cannot be taken for granted.

## SECTION 6

### CUSTOMER'S ACCEPTANCE TESTS AND REPORTING

These tests are at the discretion of the customer. It is strongly recommended that the initial tests should be consistent from procurement to procurement and lot to lot in order to verify consistency. Additional follow-on tests could be used as "burn-in" to determine the short term performance or additional mission-specific tests to reflect mission requirements.

The procurement specification must spell out in detail what acceptance tests are required, what procedures are to be followed, and what the requirements are. Temperature of the cells is critical for all tests. Ambient temperature can be very misleading since depending on the thermal environment, heat sinking, and air movement, cell temperature can vary widely from ambient temperature. The practice has been to attach thermocouples or thermistors to the cover of cells distributed through a series-connected group of cells. Cell temperature should be specified as  $\pm 2^{\circ}\text{C}$  to the designated test temperature.

The recommended initial acceptance tests include the following:

- (1) Capacity at  $22^{\circ}\text{C}$
- (2) Capacity at  $10^{\circ}\text{C}$
- (3) Overcharge at  $0^{\circ}\text{C}$  for 72 hours
- (4) Capacity at  $0^{\circ}\text{C}$
- (5) Internal resistance
- (6) Internal self discharge
- (7) Cell weight, dimensions and visual inspection

The sequence in which the tests are performed should be stated in the specification, and procedures for inactivity must be established. Generally any open circuit stand (which should be in a totally discharged state) should be limited to 72 hours, or be followed by a standard "reconditioning" procedure before continuing the acceptance test procedure.

All of the data from the acceptance testing is important. As mentioned for pre-acceptance testing, it can be very helpful if the requirement parameters are plotted as histograms and if these parameters are tracked from lot to lot. Casual review of numerical data has not proved adequate in the past. An example of the histogram data analysis is shown in Reference 6.

The Acceptance Test Procedure (ATP) used by the cell manufacturers must be in total agreement with the customer's specification. The specific acceptance test varies from program to program; in practice they are customized for programs that require specific tests on order of testing. Any deviations from the documented procedure must be reported immediately and approved by the NASA QA representative and DCMC. The manufacturer should have a standard procedure for reporting, reviewing, and disposition of all anomalies or malfunctions. Failures to meet specification requirements must be disposed by a Material Review Board (MRB) at the manufacturer's facility, at the customer's facility, or both, and include customer notification.



## **SECTION 7**

### **DOCUMENTATION OF MANUFACTURING AND TEST**

In the future, each customer's procurement will have a specification unique to the program for which the cells will be used. These specifications should be similar in format and basic requirements for manufacturing and test. They may vary in the extent of inspections and test, but they should be specific in the charge and discharge rates and may vary due to program application being either LEO, medium altitude orbit, GEO, or interplanetary mission.

The previous requirement by NASA for a Manufacturing Control Document (MCD) will now be required by the customer. The need exists for a well-documented process and quality document starting with incoming materials through delivery of the hardware. Although no longer a NASA requirement per se, the NASA customer will be responsible for assuring NASA that the NiCd cells being manufactured for aerospace have built-in quality and reliability to meet the intended mission requirements.

It is of utmost importance that the manufacturer have QA control over the entire process starting with plate making and ending with cell packing and shipping. Inspection forms and travel cards must accompany the plates and cells from start to finish. All anomalies must be documented and reported to DCMC and the NASA Contractor QA. All rework must be approved by DCMC and the NASA contractor QA representative.

The manufacturer must have data sheets for all pre-acceptance and acceptance test procedures. These data sheets should be available for review by DCMC and the NASA contractor QA representative on a real-time basis, and copies of these test data must be delivered with the cells.



## **SECTION 8**

### **HANDLING OF CELLS PRIOR TO SHIPMENT**

It has been mentioned that sealed NiCd cells are never operated without supporting the large faces of the cell case. This is required since even in normal operation the internal gas (oxygen) pressure can reach 550 kPa (80 psig), and the cell case unsupported will bulge significantly. The cell cover, bottom, and edges could also bulge at pressures above 690 kPa (100 psig), but this should not occur during normal operation.

Therefore, as soon as the cell pack is welded to the case and the gauge assembly is attached to the fill tube, the cell is placed in a clamp of aluminum plates to support the large faces. The cell must remain in the clamp until all electrical testing is completed and the cell is completely discharged. During this time the pressure gauge remains attached to the fill tube, and those individuals handling the cells should be cautioned not to pick up a cell by means of the gauge. The cell and supporting plates are heavy and the fill tube can be broken from the cover.

During pre-acceptance test and acceptance testing the cells are moved several times since some tests may be performed on "cold plates" and some in temperature chambers. Care should be taken in this movement and rearrangement of cells. Needle valves are usually attached to the gauge assembly since they are required for venting of oxygen when setting the precharge. It is recommended that pipe caps be installed on the needle valves after the precharge is set to prevent any possible leakage caused by "bumping" valves during the movement of cells.





## SECTION 9

### STORAGE AND SHIPMENT

Some procurement contracts call for "dry storage" of cells that will be activated at a future date. These cells, therefore, are not activated with KOH but are filled with helium, capped, and placed in dry storage. The storage temperature and an environment of dry nitrogen must be closely controlled for the entire period of storage. Cells have been dry stored for 10 or more years, and there is no known time limit and no documented degradation of performance.

Cells that have completed acceptance testing must be sealed by crimping and welding the fill tube (pinch off). Before this is done, however, there must be a final leak test using a mass spectrometer-type helium leak detector. A leak rate of  $<1.3 \times 10^{-4}$  Pa ( $<1 \times 10^{-6}$  torr) is a requirement to avoid a cell leak which could seriously affect the cell electrode balance and reduce life. Phenolphthalein is to be used at the ceramic-to-metal terminals and fill tube weld to check for leaks. A purple color indicates a potential electrolyte leak.

The cells are to be vapor honed (cleaned). The cell identification data (part number, lot number, serial number, code for activation date, etc.) must be electro-etched on the cell edges. The cell terminals must be "tinned," and all cells weighed and dimensions measured as part of final inspection. Finally, there must be a buyoff or approval-to-ship signed by the manufacturer's QA, by DCMC, and by the NASA Contractor's QA.



## SECTION 10

### ADVANCED DESIGN NICKEL CADMIUM AEROSPACE CELLS

Sealed NiCd cells for Spacecraft Applications will vary somewhat from various manufacturers. However, there are also some advanced design cells available that have significant differences from the design and manufacturing process that has been discussed in the previous sections.

#### 10.1 THE "SUPER" NiCd™ CELL

Hughes Aircraft Company has developed an advanced design NiCd cell (Super NiCd™) which addresses the major NiCd degradation mechanisms. Some of these design changes are summarized as follows:

- (1) Replacement of the nylon separator with an inert, polymer impregnated, zirconia separator.
- (2) Incorporation of electrochemically impregnated positives and negatives and use of an additive to reduce cadmium electrode loss.
- (3) Cell design allowing for ~33% increase in electrolyte quantity.

The incorporation of the above design modifications in boilerplate, protoflight, and flight cells have demonstrated excellent performance, especially in GEO regimes characteristic of communication satellites. An independent evaluation of this technology was implemented by NASA. The NASA evaluation consisted of monitoring the manufacture and performance of these cells during testing at the manufacturer's facility, followed by characterization and cycling of the cells at NWSC Crane. Preliminary results of the manufacturing and testing of these cells has been previously reported (Ref. 8). The cells used in this evaluation were rated at 21 Ah, and were built as an add-on to a Hughes flight lot for the LEASAT Program at the Eagle-Picher, Colorado Springs facility.

The following are changes made in the manufacture of NiCd cells to improve performance, life and reliability. The following design is a brief summary of the "SUPER" NiCd cell design.

- (1) Plates are electrochemically impregnated with nickel hydroxide and cadmium hydroxide.
- (2) The separator material is "Zircar" (zirconium oxide) rather than nylon, and contains a polymer treatment to enhance wettability and mechanical robustness.
- (3) The combination of electrochemically impregnated positive and negative plates and the separator allows for significantly more electrolyte than the 3 cc per ampere hour rule of thumb.
- (4) The cell design has almost a 1:1 height-to-width ratio, which facilitates the current distribution through the plate and makes it more uniform.

One apparent drawback for NASA's use of this cell is the proprietary electrode additive required by the manufacturer. If control of this process is verified, it will be possible to constantly manufacture and use this cell. NASA has flown and is planning to use the "SUPER" NiCd™ technology on several missions (SAMPEX, FAST, SWAS, XTE, and others).

#### 10.2 THE NASA "ADVANCED" NICKEL-CADMIUM CELL

Since many NASA missions are of the LEO type, cell design modifications which would give better performance in this type of cycling (implied from Hughes' boilerplate test data, see Ref.8) were incorporated. The following design (also referred to as the 'MAGNUM' cell by the manufacturer) is

based on the "Super NiCd" cell; however, no proprietary electrolyte additives may be used if the customer desires.

- (1) Plates are electrochemically impregnated with nickel hydroxide and cadmium hydroxide.
- (2) The separator material is polypropylene rather than nylon, and the polypropylene is filled with a polymeric additive, which enhances wettability.
- (3) The combination of electrochemical positive and negative plates and the separator provide for significantly more electrolyte than the 3 cc per ampere hour rule of thumb. In practice the cells use >4 cc/Ah.
- (4) The cell design has almost a 1:1 height-to-width ratio, which facilitates the current distribution through the plate and makes it more uniform.

#### **10.2.1 Plate Manufacture**

The process of electrochemical impregnation was described above (Section 4.2.3). It is a process similar to the nickel plating of metal hardware, in that a current flows through a number of plates in parallel and deposits nickel and cadmium hydroxide, respectively, in the electrode pores directly in the nickel/cobalt and in the cadmium nitrate solution. The concentration, temperature, acidity, and current per unit area are all critical. The time required to produce the desired loading of active material is also critical, and the impregnation may be accomplished in a single step or in several steps.

#### **10.2.2 Separator Material**

As discussed previously, nylon has serious temperature limitations. Polypropylene used in the past as a substitute for nylon had pressure problems; however, in this case, it is being used with a proprietary treatment. Zircar appears to be a more favorable material, but it also has some constraints and uses an additive in the separator material. The polypropylene separator material also uses the same additive.

#### **10.2.3 Cell Performance**

Sealed cells using electrochemically impregnated plates, treated Zircar, and polypropylene separators, and having a unique electrolyte additive, have demonstrated longer life and higher end of discharge voltages than the basic sealed NiCd cell. Cells of the 'Super Ni-Cd' type have been used in many communications satellites and several NASA LEO missions.

### **10.3 FIBER SUBSTRATE PASTED PLATE CELLS (Refs. 9-11)**

The following advanced design NiCd cell uses a plate manufacturing process that requires pasting of the active materials into a structure formed by nickel-plated polypropylene fibers. This design has been selected for several aircraft applications by an airplane manufacturer. This cell is known as the "ACME" cell. It is unique for the following reasons:

- (1) The plate substrate is neither perforated steel sheet nor nickel wire screen. The substrate is a nickel-plated polypropylene fiber mat. The nickel and cadmium active materials are pasted into the mat.
- (2) The separator material is polypropylene.
- (3) There are two cadmium plates separated by an open nickel plated fiber mat for each nickel plate, which facilitates oxygen recombination.
- (4) The cell can operate at low pressure even with excess amounts of electrolyte.

Cells of this design are still in the development stage for aerospace use, but evaluation tests have demonstrated good cycling capability using an LEO charge/discharge regime (Ref. 9). The manufacturing processes for the plates and cell fabrication, and detailed test procedures for aerospace cells of this cell design have not yet been formalized. Application of these cells has been limited to terrestrial or aircraft use, but space application appears feasible.



## **APPENDIX A**

### **CHECKLIST FOR PREPARING PROCUREMENT SPECIFICATIONS**

1. Nickel powder must meet the requirements of the cell manufacturer's procurement specification and must not be changed without customer approval.
2. The binder used in the slurry must meet the requirements of the cell manufacturer's procurement specification.
3. All water used throughout the manufacturing process must be deionized and must meet the cell manufacturer's purity specification.
4. Substrate materials: perforated nickel plated steel, nickel screen, or nickel plated fibers must meet the cell manufacturer's specification.
5. The sintering operation must be performed under controlled conditions and not changed without approval by the customer.
6. The chemicals: nickel nitrate, cobalt nitrate, cadmium nitrate, potassium hydroxide, sodium hydroxide, etc., must meet the cell manufacturer's procurement specification.
7. The impregnation operation or pasting operation must be performed under controlled conditions and not changed without approval by the customer.
8. The cell manufacturer's "Plate Acceptance and Inspection Report" must show that plate porosity is over 35%; that positive plate and negative plate thickness, plate loading, and weight are within tolerance; and that the ratio of negative plate capacity to positive plate capacity exceeds 1.5.
9. Plates must be 100% visually inspected for defects such as cracks, burrs, pinholes, edge coining, and surface conditions.
10. Both positive and negative plates must go through a process to minimize carbonates.
11. Negative plates may be Teflonated, and this must be a controlled process not changed without the approval of the customer.
12. Both positive and negative plates must be weight sorted and evaluated for uniformity and consistency.
13. All plates must be processed through a flooded cell electrical test to verify total plate capacities and the ratio of negative-to-positive capacity.
14. After the flooded cell test, all plates must again be 100% visually inspected.
15. All cell components, in addition to plates, must be subjected to incoming inspection. Terminal seals must be tested for gas leakage. Separator material must meet the cell manufacturer's specification.
16. All welding must be performed by certified individuals only, and welds must be 100% inspected.
17. Potassium hydroxide used for electrolyte must have a certified analysis and be maintained within the carbonate tolerance.
18. The amount of electrolyte must be tightly controlled and be verified by cell weight before and after addition.
19. Cells must be tested for gas leakage before any electrical tests are performed.

20. Cells must be processed through pre-acceptance (in house acceptance) testing according to the cell manufacturer's approved procedure, and this procedure must not be changed without approval by the customer.
21. The adjustment of negative "precharge" must be a controlled process and must be verifiable by test of sample cells.
22. Cell acceptance tests must conform to the customer specification and meet all requirements. Any anomalies or failures must be subjected to Material Review Board action.
23. Final inspection must include review of all acceptance test data, plus gas leakage test cell weight, and cell dimensions.
24. Each cell must have permanent identification of lot number, serial number, and date of activation, and there must be traceability from these numbers to all components and test data.
25. Packaging for shipment and method of shipment must meet customer requirements.



**APPENDIX B**  
**ACRONYMS AND ABBREVIATIONS**

Ah	ampere hour
ATP	Acceptance Test Procedure
C	ampere hour capacity
CFI	cell fabrication instructions
CQI	cell quality instructions
DCMC	Defense Contracts Management Command
DOD	depth of discharge
ECT	electrochemical test
FNC	fiber nickel cadmium
GEO	geosynchronous Earth orbit
IECEC	Intersociety Energy Conversion Engineering Conference
KOH	potassium hydroxide
kPa	kilapascal
LEO	low Earth orbit
mAh	milliampere hour
MCD	Manufacturing Control Document
MIP	mandatory inspection point
MRB	Material Review Board
NASA	National Aeronautics and Space Administration
NiCd	nickel cadmium
NWSC	Naval Weapons Support Center
PBI	polybenzimidazole
psig	Pounds per square inch gauge
QA	Quality Assurance
TIG	tungsten inert gas (welding)
Wh/kg	watt-hours per kilogram
V/T	temperature-compensated voltage



## APPENDIX C

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## APPENDIX D

### AEROSPACE NICKEL CADMIUM CELL MANUFACTURERS AND TYPICAL KEY PARAMETERS (Coded to key parameters in table)

- |  |  |
|--|--|
| <p>A    Saft Aerospace Batteries<br/>Gainesville, Florida</p> <p>B    Saft Advanced Batteries<br/>c/o Saft America<br/>Romainville, France</p> <p>C    Eagle Picher Industries<br/>Power Systems Department<br/>Colorado Springs, Colorado</p> | <p>D    Sanyo Electric Co.<br/>c/o Sanyo Energy (U.S.A.) Corp.<br/>Hyogo, Japan</p> <p>E    ACME Electric Corporation, Aerospace<br/>Division<br/>Tempe, Arizona</p> |
|--|--|

Typical Key Parameters  
(Not Specification Requirements)

Manufacturer	A	B	C	D	E
Positive Plate Loading g/dm <sup>2</sup> (g/cc void)	11.4 (2.14)	13.8 (2.06)	9.84 (1.65)	12.2 (2.43)	— (1.50)
Negative Plate Loading g/dm <sup>2</sup> (g/cc void)	15.7 (2.54)	18.0 (2.30)	17.7 (2.15)	2.06 (3.00)	— (2.16)
Positive Plate Thickness mm	0.68	0.79	0.71	0.63	1.44
Negative Plate Thickness mm	0.79	0.92	0.81	0.80	0.81 (split)
Neg/Pos Cap. Ratio by Test	1.83	1.80	1.75	1.64	2.22
Electrolyte Amount cc/Ah	2.91	3.57	4.06	2.53	>4
Cell Weight g/ Ah	37.8	32.4	40.0	27.1	33.8
Energy Density Wh/kg	31.7	37.0	33.8	44.2	35.5
Specific Energy Wh/liter	95.4	102	90.2	149	79.1



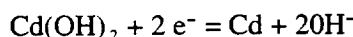
## APPENDIX E

### FREQUENTLY USED CALCULATIONS

#### A. Calculation of Theoretical Capacity

To determine the theoretical capacity of the electrodes in the NiCd cell, consider the reactions shown in Section 2.2.

Faraday's Law describes the production or reaction of 1 gram equivalent of an element or compound produces 96,494 coulombs (ampere seconds) or 26.8 ampere hours (Ah) of electricity. Therefore, with regard to the charging of  $\text{Cd}(\text{OH})_2$  to Cd in Reaction (2):

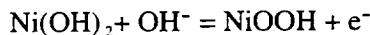


The gram equivalent weight of  $\text{Cd}(\text{OH})_2$  is:

$$[112.2 + 2(16 + 1)]/2 = 73.2$$

Thus, 26.8 Ah will be required to charge (reduce) 73.2 grams of  $\text{Cd}(\text{OH})_2$  to Cd metal in the cell.

With regard to the charging of  $\text{Ni}(\text{OH})_2$  to  $\text{NiOOH}$  Reaction (3):



The gram equivalent weight, of  $\text{Ni}(\text{OH})_2$  is:

$$[58.7 + 2(16 + 1)]/1 = 92.7$$

Thus, 26.8 Ah will be required to charge (oxidize) 92.7 grams of  $\text{Ni}(\text{OH})_2$  to  $\text{NiOOH}$  in the cell.

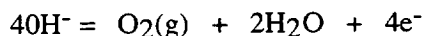
Note! It takes less  $\text{Cd}(\text{OH})_2$  (gravimetrically) to provide the 26.8 Ah than  $\text{Ni}(\text{OH})_2$ .

The calculations are for the theoretical capacity of the pure compounds. Actually  $\text{Ni}(\text{OH})_2$  is generally found in the hydrated state, e.g.,  $\text{Ni}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ . Therefore, to provide 26.8 Ah the weight of the active material will have to be increased by 18 g for each mole of hydrated water.

#### B. Calculating Gassing Rates

Oxygen is generated and hydrogen can be generated during overcharge and over discharge conditions. Oxygen is generally recombined in the cell during charge and overcharge. However, hydrogen only reacts at very slow rates. Thus, the buildup of hydrogen could result in a cell venting or bursting. Thus, the rate of gas generation becomes important.

According to Reaction (4) in Section 2.2:



Therefore, 26.8 Ah will result in generation of 1/4 mole Of  $\text{O}_2$  or  $(32 / 4) = 8$  gm of  $\text{O}_2$ .

One mole of an ideal gas (assume ideality for  $\text{O}_2$  and  $\text{H}_2$ ) at STP ( $0^\circ\text{C}$ , [1,000 Pa] 1 Atm) will occupy 22.4 liters.

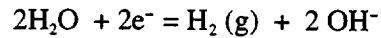
$$8/32 = x/22400 \text{ cc}$$

Thus, 8 g of O<sub>2</sub> will occupy 5600 cc. This equates to 209 cc Of O<sub>2</sub> per Ah. or 4.8 mAh per cc Of O<sub>2</sub> at 1,000 Pa (1 atmospheric) pressure. This can also be expressed as 4.8 mAh/cc-atm.

To relate this to other temperatures, use the ratio of absolute temperature, e.g., for 25°C the O<sub>2</sub> factor will be:

$$4.8 \text{ mAh / cc - atm} \{273/298\} = 4.4 \text{ mAh / cc-atm at } 25^{\circ}\text{C}$$

For the generation of H<sub>2</sub> given in Reaction (7):



26.8 Ah will produce 1/2 mole of H<sub>2</sub> gas (1 g), and occupy 11.4 liters. This equates to 425 cc per Ah or 2.4 mAh per cc-atm of H<sub>2</sub>. Converting to 25°C from 0°C results in a value of 2.2 mAh /cc-atm of H<sub>2</sub>.

The rate of pressure buildup for H<sub>2</sub> is double the rate for O<sub>2</sub> without recombination which can occur during overdischarge (cell reversal).